

# A Pilot study on the Flexural properties of vinyl ester composites filled with glass powder

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## Abstract.

Vinyl ester resin was filled with of glass powder with a view to increasing the flexural strength of the composites for civil and structural applications by a research Centre on composites, University of Southern Queensland (USQ). In order to reduce costs, the Centre wishes to fill as much glass powder as possible to the resin subject to maintaining sufficient strength of the composites in civil and structural applications. This project varies the percentage by weight of the glass powder in the composites, which are then subjected to flexural tests. The flexural strength and strain of the glass powder filled vinyl ester composites decreased with increasing filler content but the flexural modulus was highest at 20 w/t % of glass powder. Scanning Electron Microscope (SEM) was used to analyze the fractured samples and it was found that the fractured surfaces examined were correlated with the flexural properties.

## Introduction

The most common thermosets used as composite matrices are unsaturated polyesters, epoxies and vinylesters. Unsaturated polyesters dominate the market, whereas epoxies are preferred in high-performance applications. Unsaturated polyester offers an attractive combination of low price, reasonably good properties, and simple processing. However, basic unsaturated polyester formulations have drawbacks in terms of poor temperature and ultra-violet tolerance. Additives may significantly reduce these disadvantages to suit most applications. Where mechanical properties and temperature tolerance of unsaturated polyesters no longer suffice, epoxies are often used due to their significant superiority in these respects. Of course, these improved properties come at a higher price and epoxies are used most commonly in areas where cost tolerance is highest [1]. Epoxy vinyl ester range of resins (vinyl ester resins) was developed in the 1960s [2]. Vinyl esters (VE), as they are usually called, are closely related chemically to both unsaturated polyesters and epoxies and in most respects represent a compromise between the two. They were developed in an attempt to combine the fast and simple crosslinking of unsaturated polyesters with the mechanical and thermal properties of epoxies [1]. This research project is to investigate the flexural strength, maximum flexural strain and flexural modulus of vinyl ester composites reinforced with varying percentage by weights of three types of glass powder with a view to finding out the most effective amount of glass powder in strengthening the composites.

## Vinyl ester resins and their crosslinking

The polymerization product between methacrylic acid and bishphenol A is vinyl ester, which can be a highly viscous liquid at room temperature or a low melting point solid, depending on the bishphenol A used. For further processing, the polymer is dissolved in a low molecular monomer, or reactive diluent, usually styrene, the result is a low viscosity liquid referred to as resin. With the addition of a

small amount of initiator to the resin the crosslinking reaction, or curing, is initiated. The initiator used is an organic peroxide, e.g. methyl ethyl ketone peroxide (MEKP). The added amount is usually 1 to 2 percent by volume. The peroxide decomposes after it is added to the resin and the reaction is exothermic. The initiator is a molecule that produces free radicals. The free radical attacks one of the double bonds on the ends of the polymer and bonds to one of the carbon atoms, thus producing a new free radical at the other carbon atom, which illustrates the whole crosslinking process. This newly created free radical is then free to react with another double bond. Since the small monomer molecules, the styrene molecules, move much more freely within the resin than the high molecular weight polymer molecules, this double bond very likely belongs to a styrene molecule. The bridging step creates a new free radical on the styrene, which is then free to react with another double bond and so on. Health concerns with vinyl esters are considered synonymous with the most common crosslinking agent, the styrene, and not with the resins themselves. Styrene is volatile and evaporates easily and becomes an inhalation hazard. The reported levels that cause a specific acute reaction vary widely, partly because tolerance is individual and depends on build up, and partly because reactions are subjective. At concentrations in the range of 20-100 parts per million (ppm), styrene is a mild, temporary irritant to eyes and respiratory tract. Above 200 ppm styrene is a definite irritant causing central nervous system depression, and above 500 ppm it is a severe irritant.

## Glass powder

The glass powder used is [SPHERICEL® 60P18](#) which are hollow glass spheres are used for enhancing performance and reducing viscosity in paints and coatings and as lightweight additives in plastic parts. They are chemically inert, non-porous, and have very low oil absorption. Hollow Spheres are now widely used in diverse applications such as industrial explosives and as performance additives for the refractory and ceramic industries. Typical properties of the spheres are shown in Table 1 [3].

Table1: Typical properties of hollow glass spheres

<b>Glass powder type</b>	<b>SPHERICEL® 60P18</b>
Shape	Spherical
Colour	White
Composition	Proprietary Glass
Density	0.6 g/cc
Particle Size	18 microns
Hardness	6 (Moh's Scale)
Chemical Resistance	Low alkali leach/insoluble in water
Crush Strength	>10,000 psi

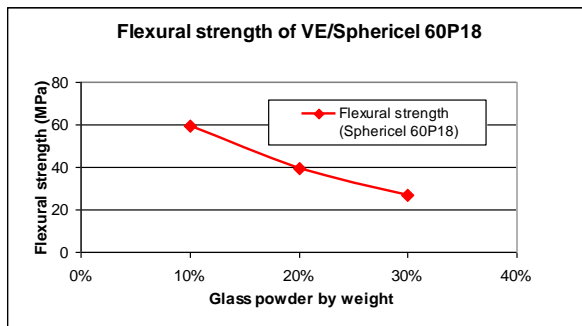
Table 2: Flexural strength, maximum flexural strain and flexural modulus of vinyl ester composites filled with Sphericel 60P18 glass spheres

\* by extrapolation # standard deviation

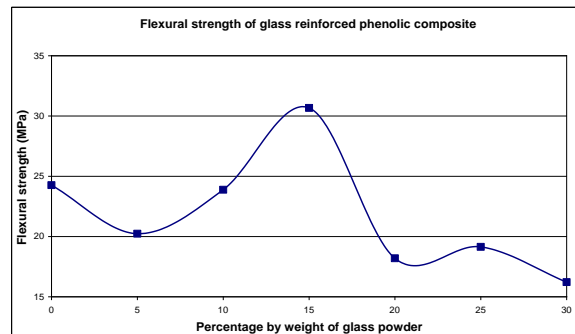
Mechanical properties	Percent by weight of glass powder	0*	10	20	30
Flexural strength (MPa)		86.22	59.53 (5.55)	39.22 (5.90)	31.02 (3.07)
Maximum flexural strain (%)		2.64	2.00 (0.29)	1.43 (0.24)	0.98 (0.09)
Flexural modulus (GPa)		3.55	2.95 (0.20)	2.76 (0.24)	3.13 (0.27)

## Results and discussions

Ray et al. filled FB-701 vinyl ester resin of Ruia Chemicals with fly ash particles [5]. It was found that the addition of fly ash particles decreased the flexural strength of the composites. Due to weak matrix/filler interaction, the filler did not accommodate the deformation force much. The value was minimum when the particulate loading was 30% and then increased gradually with more particulate loading because the smaller particles could now occupy the interstitial spaces, and consequently increasing the surface area of contact and hence the flexural strength [4]. The flexural strength of neat resin was 85.02 MPa and dropped to 32.89 MPa when the particulate loading was 30% but increased steadily to 45.98 MPa and 52.83 MPa for the 40 and 50 w/t % loaded composites respectively. At 60 % by weight of filler, the flexural strength decreased again. At such a high filler



**Figure 1: Flexural strength of Spherichel 60P18 filled vinyl ester composites with varying percentage by weight of glass powder.**



**Figure 2: Flexural strength of varying percentage by weight of glass powder reinforced phenolic resin**

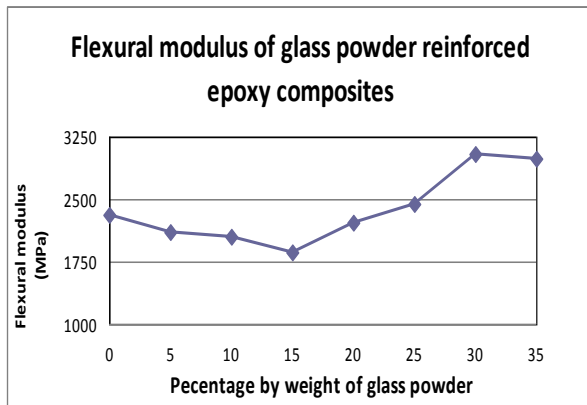
loading, the resins was not enough to encapsulate the fly ash particles completely, leading to the generation of a large number of voids, which reduced the strength. They not only reduced the stress bearing areas but also acted as stress raisers, initiating the cracks [4]. Auad et al. found that the flexural strength of neat divinyl ester resin (DVES) was 88.18 MPa, which was also not far from that obtained by Ray et al [5]. They modified the flexural properties of divinyl ester resin with carboxyl terminated poly (butadiene-co-acrylonitrile) (CTBN) and vinyl terminated poly (butadiene-co-acrylonitrile) (VTBN) respectively. It was found that for both types of rubber, the flexural strengths increased slightly up to 5 % by weight of modifiers. They then dropped either moderately for VTBN modified composites or drastically for CBTN modified composites. For VTBN modified composite, the flexural strength increased again after 7.5 % by weight of reinforcer [5].

Figure 1 shows the flexural strength of Spherichel 60P18 filled epoxy composites. By extrapolation, it can be found that the flexural strength of neat resin in this study was 86.22 MPa which was a little bit higher than that found by Ray et al. but a bit lower than that found by Auad et al. but not much. It can therefore be argued that it is pretty accurate. The values of the flexural strength then dropped progressively with increasing particulate loading, up to 30 % by weight of particulate, as those in Ray et al.'s case. It can be argued that when the particulate loading was increased to over 30 % by weight, the flexural strength in this study would climb to a maximum and then dropped back as in Ray et al.'s study. Moreover, Ku et al. discovered a similar trend when phenolic resin was reinforced with varying percentage of Spherichel 60P18, glass powder as depicted in Figure 2 [6]. Sen and Nugay observed similar behaviour for the tensile strength of fly ash filled polyester composites and concluded that the presence of voids and the formation of air bubbles were responsible for the lowering of the strength [7]. Table 2 shows the flexural strength, strain and modulus of Spherichel 60P18 glass spheres filled vinyl ester composites with varying particulate loading and standard deviations. Figure 3 shows the flexural modulus of glass powder filled epoxy composites. The trend of the values of the flexural modulus was the same with that of this study and that of Ray et al.. The minimum value of flexural strength occurred at 15 % by weight of particulate loading; it then rose back to a maximum at 30 w/t % of filler before dropping down with higher particulate loading [8].

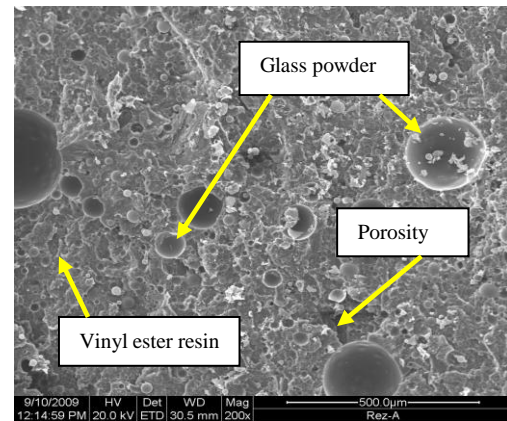
Figure 4 is the SEM image of 10% by weight of Spherichel 60P18 filled vinyl ester composite and the amount of porosity in the specimen was quite low due to the abundance of vinyl ester resin, which in turn gave it a high flexural strength. References

## Conclusions

This study has evaluated the flexural strength, strain and modulus of varying percentages by weight of glass powder reinforced vinyl ester resin. The flexural strength values of glass spheres decreased with



**Figure 3: Flexural modulus of glass powder filled epoxy composites**



**Figure 4: SEM image of 10% by weight of Sphericerl 60P18 filled VE composite, 200 X**

increasing particulate loading. The values of the flexural strain had the same trend as that of flexural strengths. On the other hand, the flexural moduli dropped slowly to a low value at 10 to 20 percent by weight of filler but then rose steeply to a value higher than that of neat resin at around 50 % particulate loading but then dropped back with further particulate loading. It can be argued that when the fusion between vinyl resin (matrix) and glass powder (reinforcer) is improved by adding some other filler, e.g. barium sulfate and other resins to the composites, its flexural strength and modulus will be improved.

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